Exicton effect of resonant Raman spectra in two-dimensional materials

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論　文　内　容　要　旨

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氏　　名	白倉　俊哉	提出年	平成 30　年
学位論文の 題　　目	Excition effect of resonant Raman spectra in two-dimensional materials (2 次元物質における共鳴ラマンスペクトルの励起子効果)		

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Background

The electron configuration of a molybdenum and sulfur atoms for MoS_2 that contributes to the optical properties are $5s_1 4d_5$ and $3s_2 3p_4$, respectively. The electronic states MX_2 (M= Mo, W, and X= S, Se and Te) in the lowest conduction band and in the top valence band are dominated by component of p orbital of X atoms and d orbital of M atom which form a planar hexagonal lattice. The MX_2 single layer is made of transition metal atom sandwiched by chalcogen atoms. By stacking layers of TMDs we get three dimensional crystal structure. Between the layers there are weak van der Waals interaction, which allows layers of TMDs to be easily exfoliated, or to slide in the direction parallel to the plane.

Let us discuss Raman spectra of monolayer MoS_2. Monolayer MoS_2 are mechanically exfoliated from bulk crystals onto 90 nm SiO_2. The mono-layer MoS_2 is identified using atomic force microscopy (AFM) and resonance Raman measurements. AFM measurement on monolayers shows a height of 0.7 nm corresponding to the thickness of a single MoS_2 layer (1L). From the bulk to monolayer MoS_2, the out-of-plane Raman mode (A_1) softens and the in-plane mode (E') does not change the position of Raman shift. We introduce the excitation energy dependence of Raman intensity measurement. The relative intensities of these modes depend on the excitation energy. The A_1 mode

is more intense than the E' phonon mode for laser energies from 1.92 eV to 2.8 eV.

Purpose

Raman spectroscopy has been used frequently for two-dimension (2D) materials. However, no theoretical model considered for a role of the exciton in resonant Raman spectra of the 2D materials, because of the high computational cost of many-body perturbation theory calculations of excitons and the implementations to resonant Raman spectra that unify electron-phonon and many-body phenomenons first principle calculations. In this thesis, we develop a simple tight binding approach by adopting maximally localized Wannier function (MLWF) basis functions obtained by density functional theory (DFT). This framework is crucial to capturing excitonic effect of resonant Raman scattering in MoS_2, including the relative Raman intensity for several Raman peaks as a function of photon energy, in particular for the A, B and C exciton energies. The purpose of this thesis is to reproduce resonant Raman spectra for different incident excitation laser energies by considering the exciton wave functions. We show that band-extrema electron-hole pairs such as the A and B excitons suppress the Raman response. Further, in the parallel-band electron-hole pairs such as the C exciton enhances the Raman response due to their bunching up energies that makes strong exciton-phonon coupling during the atomic vibration.

Methods

We employ both numerical and analytical methods to obtain resonance Raman spectra of two-dimensional semiconductors. Using the perturbation theory and DFT calculations, we calculate the exciton-photon, exciton-phonon matrix elements of monolayer MoS_2. Using the numeric approach based on tight binding model based on the Maximally localized Wannier functions, we derive a directly Bethe-Salpeter equation to calculate exciton effect of resonance Raman intensity.

Results and Summary

In this thesis, we have discussed the theoretical calculation for the excitonic effect of resonance Raman scattering in transition metal diechalcogenide, in particular, monolayer MoS_2. The calculated results are compared with the experimental measurements. The calculation have been performed in the

k-space particularly (1) near the K point and (2) in the central region of the Brillouin zone between the point and the K point which correspond to the observation of the A, B excitons and the C exciton, respectively. In order to understand the excitonic effect of resonant Raman spectra, we need information of the electronic structure, excitonic optical matrix elements, phonon modes and exciton-phonon matrix elements that are given by using the Bethe-Salpeter equation from tight binding approach. In this study, we drive formula to calculate the exciton wave function based on the maximally-localized Wannier functions. Then, we make our original program codes to calculate exciton-photon matrix element and exciton-phonon coupling. The eigenvalues and eigenvectors of the electronic structure and phonon modes are obtained by the Quantum Espresso andWannier90 packages. Our finding can be divided in two parts:

The relative resonant Raman intensity between the in-plane and out-of-plane phonon modes is studied as a function of the excitation laser energy for understanding the excitonic effect of the resonance Raman intensity of monolayer MoS_2. We have calculated the exciton energy dependence of the Raman intensity for the E'and A_1phonon modes, which nicely reproduces the resonant Raman measurement. Based on the present calculations, we conclude that the relative intensity of the A_{1g}phonon mode in monolayer MoS_2 from 1.92 eV to 2.81 eV of excitation laser energies is stronger than that of the E′phonon mode by calculating exciton-phonon coupling even when we change the excitation laser energy. The origin of this observation is explained by the effects of the resonant Raman scattering in monolayer $MoS_2$with A, B and C excitons. This fact can be explained by the exciton-phonon matrix elements for the E′mode and the A_1mode for 1.92 eV, 2.18 eV and 2.8 eV laser excitation energy.

The excitonic optical transition as a function of laser energy $E_L$has three peak values at E_L= 1.92 eV, 2.18 eV and 2.8 eV that is corresponding to A, B and C exitions, respectively. We evaluate the resonance Raman intensity of the E′and the A1phonon modes as a function of the excitation laser energy by considering excitonic effects. We conclude that the resonance Raman intensity of the A_1phonon mode strongly enhanced by C exciton than the A or B excitons. The peak value of Raman intensity for the A

(1.92 eV) and B (2.18 eV) exciton is about 5 times smaller than that of C

exciton. The reason is that the peak intensity value is mainly determined by the fourth power of the absolute value of exciton-photon matrix element. As we compare exiciton-photon optical transition between A, B and excitons, the peak value of optical absorption for the A and B excitons is 1.5 times smaller than that of C excitons peak value.

By understanding the exciton-phonon transitions in the Raman spectra of monolayer MoS_2, we expect that more detailed exciton-phonon interaction can be observed in the future experiments.

別　紙

論文審査の結果の要旨

近年、厚さが１原子層である２次元物質が従来にない顕著な物理的性質を示すことから、精力的に研究が行われている。新規２次元物質の構造や電子状態を理解するために、共鳴ラマン分光がよく用いられる。共鳴ラマン分光では、励起レーザー光によって２次元物質中に、電子と正孔の対が発生する。電子と正孔の間のクーロン力によって束縛状態である励起子が発生するが、２次元物質の場合には励起子の束縛エネルギーが３次元物質に比べて大きいので、励起子が室温でも存在する。このため２次元物質の共鳴ラマンスペクトルを理解するためには、２次元励起子の共鳴ラマンスペクトルに与える効果を議論する必要性がある。

白倉俊哉氏提出の博士論文は、(1)２次元物質の励起子状態を比較的短時間で計算するために、実空間で局在したワニエ関数を基底として解くプログラムを開発し、また(2)計算によって得られた励起子波動関数を用いて、共鳴ラマン分光スペクトルを計算するプログラムを開発している。この結果、２次元物質の共鳴ラマン分光の励起子効果について理論的に知見を与えたものである。本論文の第１章では、本論文の目的と背景が述べられている。第２章では、励起子状態を計算するための基礎方程式であるベーテサルピータ方程式を、局在したワニエ関数を基底として求める計算手法が述べられている。第３章では、空間に局在したワニエ関数を用いて、電子と光子との相互作用また電子と格子との相互作用を計算する手法が述べられている。第４章では、具体的に２次元物質における MoS_2 の電子格子相互作用の行列の計算結果、ならびに励起子効果を入れた電子格子相互作用の結果が示されている。第５章では、励起子効果を取り入れた、電子光子相互作用、電子格子相互作用の値を用いて共鳴ラマン分光スペクトルの数値計算の結果が示されている。第６章では本論文で得た結論をまとめている。

本論文で得られた結果は、２次元物質の励起子状態の計算に関して新しい知見をもたらすだけでなく、励起子効果を取り入れた共鳴ラマンスペクトルを第一原理計算で計算する手法の開発を実現し、実験と比較することを可能にした。このことは白倉氏が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示したものである。したがって、白倉氏提出の論文は博士（理学）の学位論文として合格と認める。